



Nanoclay and swift heavy ions induced piezoelectric and conducting nanochannel based polymeric membrane for fuel cell



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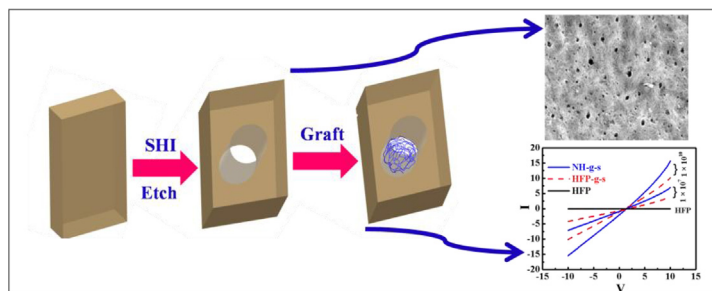
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HIGHLIGHTS

- Through nanochannels have been created using swift heavy ion and selective etching.
- Nanochannels have been functionalized with ion conducting polymer.
- Membranes are tested using DMFC and found excellent for fuel cell.
- Mechanism of ion conduction through membrane has been established.

GRAPHICAL ABSTRACT



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ABSTRACT

Through nanochannels are fabricated in poly(vinylidene fluoride-co-hexafluoro propylene) films by bombarding swift heavy ions (SHI) of energy 80 MeV and thereby creating latent tracks in the ion passage followed by chemical etching of the amorphous track. The dimension of the nanochannel is varied from 34 to 65 nm using different fluences and by dispersing organically modified nanoclay in polymer matrix. The nanochannels are grafted with polystyrene using the free radicals caused by SHI irradiation followed by their sulfonation. Nanoclay nucleates piezoelectric β -phase in copolymer whose extent gets enhanced after irradiation, grafting and sulfonation leading to a better material. The efficiency of functionalized nanochannel conduction is studied through dc conductivity of the bulk film in the semiconducting range against the insulating nature of the pristine copolymer. Current-voltage (I - V) characteristic of the membrane exhibits strong fluence dependency and shows superior conduction in functionalized nanohybrid. Proton conductivity of the functionalized nanohybrid is $6.2 \times 10^{-2} \text{ S cm}^{-1}$, while methanol permeability drastically reduces indicating higher values of the selective parameter of the developed membrane as compared to Nafion. Membrane electrode assembly studies of functionalized nanohybrid show 0.63 V as open circuit voltage leading to power density of 30.8 mW/cm^2 , considerably higher than the functionalized copolymer.

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1. Introduction

Several techniques have been proposed in the literature to introduce hydrophilic groups on the hydrophobic polymeric hybrid membrane. Amongst them, proton conducting membranes for fuel cell application using radiation technique is most promising [1–3]. Swift heavy ions (SHI) irradiation is one of the promising approaches because the particles lose most of its energy when passing through a film of macromolecules through electronic excitation and atomic collision [4]. Therefore, SHI create stable free radicals and nanometer dimension latent track (10–100 nm) down the path of the ions which become predominantly an amorphous zone. This damaged zone (amorphous) part can be converted into nanochannels through controlled chemical etching [5,6]. The channel size and shape may be conical, circular, cylindrical or funnel-like and depends on many factors such as linear energy transfer (LET), size of the ions, etching condition etc. [7]. The high LET of the irradiated ions generate free radicals which become the activated sites after chemical etching and LET generally depends on the mass of ions, energy and nature of macromolecules as well [8–10]. The free radicals caused by SHI bombardment are stable and remain active for long time even after etching. The surface free radicals get oxidized but the bulk free radicals remain active around the channel walls which have potential to initiate chain propagation within the channel when allowed to react with vinyl monomer and can form graft copolymer onto the pristine polymer chain [11]. The swift heavy ion bombardment can affect the physical, chemical and structural changes of macromolecules, i.e. double bond formation, chain scission, cross-linking of polymer chains and evolution of some gasses and all the characteristic changes strongly depend on chemical nature of the polymer [12]. Nonceramic piezoelectric, thermoplastic and nonreactive fluoropolymer like poly(vinylidene fluoride-co-hexafluoro propylene) (HFP) copolymer is extremely important with its high electrostrictive response and less crystallinity as compared to poly(vinylidene fluoride) homopolymer but both has similar crystalline structure [13]. Hydrophobic and high dielectric constant fluoropolymers (PVDF and HFP) exist in five crystalline forms such as α , β , γ , δ and ϵ [14]. The orthorhombic structure of β -phase with all trans conformation (TTTT) having high dipole moment of 7.0×10^{-30} Cm/repeat unit exhibits piezoelectric behavior while the γ -phase ($T_3GT_3\bar{G}$) conformation shows higher melting temperature as compared to α - and β -conformation [15]. Incorporation of high surface area, nanometer-size filler and nucleating agents like CNT, organically modified layered silicate, montmorillonite and graphene into the polymer matrix can dramatically alter their crystallization behavior, mechanical strength, thermal and gas barrier properties [16,17]. It has been observed that many composites or functionalized materials maintain the optimum dielectric loss and high dielectric constant [18]. Recently, polymeric hybrid membrane becomes one of the key materials for energy conversion technologies as it facilitates improvement in gas permeability, ultrafiltration, microfiltration and proton exchange membrane for fuel cell application with respect to its pristine polymer [19–21]. Researchers have developed alternative new membrane having hydrophilic groups attached on hydrophobic polymer chains through functionalization. Sulfonation technique using chlorosulfonic, perfluorosulfonic and polystyrene sulfonic acids are widely used to produce graft copolymer membranes [22–24]. So, our main aim is to use a technique where nanochannels can be created using swift heavy ions after suitably chemical etching the irradiated films followed by grafting within the channel. Further, functionalization through sulfonation reaction makes the channels electrically conducting for their usefulness in fuel cell application. The gas permeability, dielectric and conductivity of the hybrid membrane are also reported.

2. Experimental section

2.1. Materials

Commercial, SOLEF 11008 copolymer of vinylidene fluoride and hexafluoro propylene was used for this investigation and the polymer was supplied by Ausimont, Italy. The copolymer will be termed as HFP. Layered silicate Cloisite 30B clay, [bis(hydroxyethyl) methyl tallow ammonium ion exchanged montmorillonite] was purchased from Southern clay, USA, CEC 110 meq/100 g. Tallow is a mixture of C_{16} and C_{18} long chain alkenes. Potassium permanganate ($KMnO_4$) and sodium hydroxide (NaOH) (LOBA Chemie) were used as etchant, potassium metabisulphite $K_2S_2O_5$, (Sigma–Aldrich) was used for the cleaning purpose. The styrene monomer (Sigma–Aldrich) and toluene (LOBA Chemie) were used for grafting and were distilled before polymerization. Chlorosulfonic acid ($ClSO_3H$, LOBA Chemie) was used for sulfonation on grafted species.

2.2. Nanohybrids preparation by melt extrusion technique

Initially, HFP powder was prepared from its beads using a home-built chip sizer. Before put into the extruder, an appropriate amount of HFP powder and nanoclay (4 wt.%) were mixed using a high speed mixer (1000 rpm) and kept for 20 min. Finally, the nanohybrids were prepared through melt extrusion technique using a twin-screw extruder (Hakke Mini Lab) for 10 min at 200 °C with a shear rate of 100 rpm. Henceforth, the nanohybrids of HFP will be termed as “NH” for 4 wt.% of nanoclay in the pristine polymer. The matrix polymer HFP and extruded nanohybrid (NH) were melt processed to make thin film of 30 μ m thickness of dimension 1×1 cm² using a hot press compression molding machine (S. D. Scientific Ltd.) for ready use in irradiation experiment.

2.3. Development of channel by swift heavy ion

The irradiations experiments were performed on 30 μ m thick films using 80 MeV SHI of Si^{7+} in Inter University Accelerator Center, New Delhi, India, of both HFP and its nanohybrid (NH) samples. The samples have been irradiated at two different fluences at 1×10^7 and 1×10^{10} ions/cm² to check the effect of fluence on membrane properties in a vacuum of 5×10^{-6} mbar. The polymer thin film was taken in such a way that the range of the incident ions is greater than the film thickness of polymer, which was calculated using stopping range of ions in materials (SRIM calculation)¹². For fuel cell measurement, 4×4 cm² specimens were used to expose at low fluence of 1×10^7 ions/cm². SHI were scattered using thin gold foil in general purpose scattering chamber (GPSC). For high fluence (1×10^{10} ions/cm²) straight ion beam was scanned in an area of 10×10 mm². The irradiated films were chemically etched using an aqueous solution of alkaline etchant and oxidizing agent (9 mol L^{-1} NaOH + 0.25 mol L^{-1} $KMnO_4$) for 3 h to create the nanochannels (both HFP and its nanohybrid films) and the etched films were rapidly washed in distilled water [11]. The residual water at the surface of the thin film was absorbed with a filter paper and was dried at 60 °C for 12 h in an oven under reduced pressure.

2.4. Functionalization of channel

The porous etched films were immediately engrossed in a monomer solution containing styrene in toluene to initiate the grafting process. Solutions containing the films were purged with nitrogen before and throughout the reaction with stirring in an oil bath at 65 °C for 16 h. After the completion of graft polymerization, the unwanted homopolymer (polystyrene) was washed away by performing reflux using toluene in a soxhlet apparatus for 18 h.

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